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APRO3 E800550-1 D00192 ____P01/7700 0.00-0308720.2

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P.88549 PEJ

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- 3. Full name, address and postcode of the or of each applicant (underline all surnames)

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4. Title of the invention

0308720.2

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SUNSCREENS

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

J.A. KEMP & CO.

14 South Square Gray's Inn London WC1R 5JJ

Patents ADP number (If you know it)

026021

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 Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

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I/We request the grant of a patent on the basis of this application.

Signature Date

J.A. KEMP & CO.

Date 15 April 2003

Name and daytime telephone number of person to contact in the United Kingdom

ELLIS-JONES, Patrick George Armine 020 7405 3292

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SUNSCREENS

The present invention relates to UV screening compositions suitable for cosmetic use.

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The effects associated with exposure to sunlight are well known. Thus exposure of the skin to UVA and UVB light may result in, for example, sunburn, premature ageing and skin cancer.

Commercial sunscreens generally contain components which are able to reflect and/or absorb UV light. These components include, for example, inorganic oxides such as zinc oxide and titanium dioxide as well as organic sunscreen agents.

The general public are generally more concerned by the obvious effects of sunlight, namely sunburn which causes reddening of the skin than they are with other effects of sunlight which are less self evident. As a consequence of this commercial sunscreen compositions are rated by a Sun Protection Factor (SPF). This is a measure of the time taken for skin to redden under a layer of the composition as compared with untreated skin. Thus an SPF of 20 indicates that skin will take 20 times longer to redden under a layer of the composition applied at 2mg per cm² compared with untreated skin. This reddening effect is caused principally by UVB light. There is no recognised corresponding factor for the effects of UVA light even though the latter may be more damaging in the long term.

Most organic sunscreen agents absorb light over only a part of the UVA-UVB spectrum with the result that if one is to obtain a screening effect covering the whole UVA-UVB spectrum it is generally necessary to use a combination of different organic sunscreen agents. Some organic sunscreen agents and other components of sunscreen compositions are stable to UV light but others are photosensitive and/or may after being excited by UV light degrade another ingredient of the composition.

Titanium dioxide and zinc oxide are generally formulated as "micronised" or "ultrafine" (20-50 nm) particles (so-called microreflectors) because particles whose size is less than 10% of the wavelength of the incident light scatter light according to Rayleigh's Law, whereby the intensity of scattered light is inversely proportional to the fourth power of the wavelength. Consequently, they scatter UVB light (with a

wavelength of from 280 or 290 to 315/320 nm) and UVA light (with a wavelength of from 315/320 to 400 nm) more than the longer, visible wavelengths, preventing sunburn whilst remaining invisible on the skin.

However, titanium dioxide and zinc oxide also absorb UV light efficiently,

leading via the initial formation of electron hole pairs to the formation of superoxide and hydroxyl radicals and which may in turn initiate damage to other components of the composition. The crystalline forms of TiO₂, anatase and rutile, are semiconductors with band gap energies of about 3.23 and 3.06 eV respectively, corresponding to light of about 385 nm and 400 nm (1 eV corresponds to 8066 cm⁻¹).

Indeed there is evidence to suggest that TiO₂ can enhance the degradation of organic sunscreen agents, including UVA organic sunscreens, for example oxybenzone. Attempts have been made to reduce the adverse effects of TiO₂ and ZnO by coating but coatings are not invariably effective.

The reason why a sunscreen agent does not have a substantially perpetual effect (i.e. an SPF factor which is substantially infinite) is because the organic sunscreen agents are degraded by light and/or are adversely affected by other components of the sunscreen composition once the latter are subjected to UV light.

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It has now surprisingly been found, according to the present invention, that the degradation of organic sunscreen agents, and other components which are susceptible to degradation, can be retarded if the compositions also have present reduced zinc oxide. In other words by using reduced zinc oxide rather than ordinary zinc oxide it is, for example, possible either to provide a composition which gives better protection against UV light for the same quantity of organic sunscreen agent or a composition having the same screening effect against UV light but containing a smaller quantity of organic sunscreen agent.

Accordingly the present invention provides a cosmetic UV sunscreening composition which comprises an amount of one or more organic components which are photosensitive and/or which are degraded by another ingredient of the composition, optionally together with an amount of TiO₂ and/or ZnO and an amount of reduced ZnO, this composition having a rate of loss of UV absorption at least 5%

-3less than that of a composition having the same formulation except that it does not

contain the reduced ZnO. Thus if the rate of loss of UV absorption over at least a proportion of the UVA and/or UVB spectrum is X then the amount of the organic component(s) which are photosensitive and/or which are degraded by another 5 ingredient of the composition, optionally together with the amount of (ordinary) ZnO, possesses a said rate of loss of Y where Y is greater than X by at least 5%, and the amount of reduced ZnO reduces the said rate of loss from Y to X. The present invention also provides the use of reduced ZnO to reduce the concentration of one or more organic UV sunscreen or other photosensitive ingredient or ingredient which is degraded by another ingredient of the composition in a cosmetic UV screening composition as well as to reduce the rate of loss in UV absorption of a sunscreen composition containing one or more organic UV sunscreen agents. The present invention further provides a method of increasing the effectiveness of an organic sunscreening composition which comprises one or more components which are photosensitive and/or which are degraded by another ingredient of the composition which comprises incorporating into the composition reduced ZnO.

By "cosmetic UV sunscreening composition" is meant any cosmetic composition having UV sunscreening activity i.e. it includes compositions whose principal function may not be sunscreening. It will be appreciated that the doped TiO₂/ZnO may be the only ingredient of the composition having UV sunscreening activity i.e. the composition need not necessarily contain an organic UV sunscreen agent.

The organic component which is photosensitive or degraded by another ingredient of the composition is generally a UV sunscreen agent. Although all organic sunscreen agents which suffer a loss in UV absorption can be used, the present invention is particularly useful for agents which absorb in the UVA region. However, other organic components will generally be susceptible to free radical attack and in turn this generally will cause degradation of the UV sunscreen agent.

As indicated above the UV absorption of an organic sunscreen agent decreases with time. In contrast the UV absorption of ZnO does not decrease with

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time, or does so to a lesser extent. Since ZnO absorbs in both the UVA and UVB region whereas an organic sunscreen agent is generally more wavelength specific it can be seen that the rate of change of the UVA/UVB absorption ratio may increase over time. When reduced ZnO is used rather than the same quantity of ordinary ZnO the rate of change is reduced. This is because the doped material will enhance the performance of the organic sunscreen agent over time. Thus with a UVA sunscreen the loss of UVA absorption over time is reduced (i.e. the UVA response is more stable when the reduced material is present) so that the ratio of change of the ratio is reduced. Thus if the initial ratio of absorption is $\frac{X}{Y}$ becomes $\frac{X-x}{y}$ where x is

smaller when a reduced material is used with the result that the rate of change is less. 10 With a UVB sunscreen, the rate of change is also reduced as a consequence of a more stable UVB response.

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The rate of loss of absorption can be determined by illuminating a sample of the composition with and without the reduced ZnO of defined thickness with UV light of the appropriate wavelength and determining the absorption of UV by the composition over a given period, typically 60 minutes, obtaining a plot over that period for the wavelengths in question and determining the area under the curve from which the rate of loss can be calculated. Clearly the smaller the area under the curve the smaller the loss. For UVA absorption wavelengths from 320 to 400, especially from 340 to 390 nm, are considered.

While any reduction in the loss of UV absorption is an advantage, it is generally desirable that the presence of the doped oxide should reduce the rate of UV absorption by an amount of at least a 5%, preferably at least 10%, more preferably at least 15%, especially at least 20% and most preferably at least 40%.

The average primary particle size of the particles is generally from about 1 to 200 nm, for example about 1 to 150 nm, preferably from about 1 to 100 nm, more preferably from about 1 to 50 nm and most preferably from about 20 to 50 nm. The particle size is preferably chosen to avoid colouration of the final product.

Where particles are substantially spherical then particle size will be taken to

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represent the diameter. However, the invention also encompasses particles which are non-spherical and in such cases the particle size refers to the largest dimension.

Reduced zinc oxide particles (i.e. particles which possess an excess of zinc ions relative to the oxygen ions) may be readily obtained by heating zinc oxide particles in a reducing atmosphere to obtain reduced zinc oxide particles which absorb UV light, especially UV light having a wavelength below 390 nm, and remit in the green, preferably at about 500 nm. It will be understood that the reduced zinc oxide particles will contain reduced zinc oxide consistent with minimising migration to the surface of the particles of electrons and/or positively charged holes such that when said particles are exposed to UV light in an aqueous environment the production of hydroxyl radicals is substantially reduced as discussed above.

The reducing atmosphere can be air with a reduced oxygen content or an increased hydrogen content but is preferably a mixture of hydrogen and an inert gas such as nitrogen or argon. Typically the concubation of hydrogen is from 1 to 20%, especially 5 to 15%, by volume, with the balance inert gas, especially nitrogen. A preferred reducing atmosphere is about 10% hydrogen and about 90% nitrogen by volume. The zinc oxide is heated in this atmosphere at, say, 500° to 1000°C, generally 750 to 850°C, for example about 800°C, for 5 to 60 minutes, generally 10 to 30 minutes. Typically it is heated to about 800°C for about 20 minutes.

It is believed that the reduced zinc oxide particles possess an excess of Zn^{2+} ions within the absorbing core. These are localised states and as such may exist within the band gap. A further discussion of this can be found in WO 99/60994.

The zinc oxide particles used in the present invention may have an inorganic or organic coating. For example, the particles may be coated with oxides of elements such as aluminium, zirconium or silicon. The particles of metal oxide may also be coated with one or more organic materials such as polyols, amines, alkanolamines, polymeric organic silicon compounds, for example, RSi[{OSi(Me)₂}xOR¹]₃ where R is C₁-C₁₀ alkyl, R¹ is methyl or ethyl and x is an integer of from 4 to 12, hydrophilic polymers such as polyacrylamide, polyacrylic acid, carboxymethyl cellulose and xanthan gum or surfactants such as, for example, TOPO.

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The compositions of the present invention may be, for example, lipsticks, skin anti-ageing compositions in the form of, for example, creams, exfoliating preparations including scrubs, creams and lotions, skin lightening compositions in the form of, for example, face powders and creams, preparations for the hands including creams and lotions, moisturising preparations, compositions for protecting the hair such as conditioners, shampoos and hair lacquers as well as hair masks and gels, skin cleansing compositions including wipes, lotions and gels, eye shadow and blushers, skin toners and serums as well as washing products such as shower gels, bath products including bubble baths, bath oils, but, preferably, sunscreens. In this connection we should point out that the expression "cosmetic UV sunscreening composition", as used herein, includes any composition applied to the skin which may leave a residue on the skin such as some washing products. Compositions of the present invention may be employed as any conventional formulation providing protection from UV light.

Organic sunscreen agents which can be used in the compositions of the present invention include any conventional sunscreen agent which gives protection against UV light while if there is no other photosensitive component the sunscreen agent is photosensitive and/or is degraded by another ingredient of the composition. Suitable sunscreen agents are listed in the IARC Handbook of Cancer Prevention, vol. 5, Sunscreens, published by the International Agency for research on cancer, Lyon, 2001 and include:

- (a) Para-aminobenzoic acids (PABA), (UVB absorbers) esters and derivatives thereof, for example amyldimethyl-; ethyldihydroxypropyl-; ethylhexyl dimethyl-; ethyl-; glyceryl-; and 4bis-(polyethoxy)- PABA.
- (b) Cinnamates (UVB) especially esters including methyl cinnamate esters and methoxycinnamate esters such as octylmethoxy cinnamate, ethyl methoxycinnamate, especially 2-ethylhexyl paramethoxycinnamate, isoamyl p-methoxy cinnamate, or a mixture thereof with diisopropyl cinnamate, 2-ethoxyethyl -4-

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methoxycinnamate, DEA-methoxycinnamate (diethanolamine salt of para-methoxy hydroxycinnamate) or α,β -di-(para-methoxycinnamoyl)a'-(2-ethylhexanoyl)-glycerin, as well as diisopropyl methylcinnamate; benzophenones (UVA) such as 2,4-dihydroxy-; 2-hydroxy-4-methoxy; (c) 5 2,2'-dihydroxy-4,4'-dimethoxy-; 2,2'-dihydroxy-4-methoxy-; 2,2',4,4'tetrahydroxy-; and 2-hydroxy-4-methoxy-4'-methyl-benzophenones, benzenesulphonic acid and its sodium salt; sodium 2,2'-dihydroxy-4,4'-dimethoxy-5-sulphobenzophenone and oxybenzone; (d) dibenzoylmethanes (UVA) such as butyl methoxydibenzoyl methane, 10 especially 4-tert-butyl-4'methoxydibenzoylmethane; (e) 2-phenylbenzimidazole-5 sulfonic acid UVB and phenyldibenzimidazole sulfonic acid and their salts; (f) alkyl- β , β -diphenylacrylates (UVB) for example alkyl α -cyano- β , β diphenylacrylates such as octocrylene; triazines (UVB) such as 2,4,6-trianilino-(p-carbo-2-ethyl-hexyl-1-15 (g) oxy)-1,3,5 triazine as well as octyl triazone e.g. ethylhexyltriazone and diethylhexyl butamido triazone. (h) camphor derivatives (generally UVB) such as 4-methylbenzylidene and 3-benzylidene- camphor and terephthalylidene dicamphor 20 sulphonic acid (UVA), benzylidene camphor sulphonic acid, camphor benzalkonium methosulphate and polyacrylamidomethyl benzylidene camphor; organic pigment sunscreening agents such as methylene bis-(i) benzotriazole tetramethyl butylphenol; 25 (j) silicone based sunscreening agents such as dimethicodiethyl benzal malonate. (k) salicylates (UVB) such as dipropylene glycol-; ethylene glycol-, ethylhexyl-, isopropylbenzyl-, methyl-, phenyl-, 3,3,5-trimethyl- and TEA-salicylate (compound of 2-hydroxybenzoic acid and 2,2'2"-30 nitrilotris (ethanol));

(l) anthranilates (UVA) such as menthyl anthranilate as well as bisymidazylate (UVA), dialkyl trioleate (UVB), 5-methyl-2-phenylbenzoxazole (UVB) and urocanic acid (UVB).

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Some compounds are effective for both UVA and UVB. These include anisotriazine, methylene bisbenzotriazolyl tetramethylbutyl- phenol and drometrizole trisiloxane (Mexoryl XL).

The organic sunscreen agent(s) are typically present in the compositions at a concentration from 0.1 to 20%, preferably 1 to 10%, and especially 2 to 5%, by weight based on the weight of the composition.

In the compositions the reduced zinc oxide is preferably present at a concentration of about 0.5 to 20 % by weight, preferably about 1 to 10 % by weight and more preferably about 3 to 8 % by weight, in particular about 4 to 7%, such as 4 to 6% for example about 5%, by weight.

The compositions may be in the form of, for example, lotions, e.g. thickened lotions, gels, vesicular dispersions, creams, milks, powders, solid sticks, and may be optionally packaged as aerosols and provided in the form of foams or sprays.

The compositions may contain any of the ingredients used in such formulations including fatty substances, organic solvents, silicones, thickeners, demulcents, other UVA, UVB or broad-band sunscreen agents, antifoaming agents, moisturizing agents, perfumes, preservatives, surface-active agents, fillers, sequesterants, anionic, cationic, nonionic or amphoteric polymers or mixtures thereof, propellants, alkalizing or acidifying agents, colorants and metal oxide pigments with a particle size of from 100 nm to 20000 nm such as iron oxides along with conventional (undoped) TiO₂ and ZnO.

It is known that other ingredients of cosmetic compositions, for example some surface-active agents may have the effect of degrading certain sunscreen agents in the presence of UV light. Also TiO₂ and ZnO are known to degrade certain organic sunscreens such as oxybenzone as well as antioxidants such as vitamins e.g. vitamins A, B, C and E. It will be appreciated that is particularly useful to use the reduced ZnO with such sunscreens. This is because ZnO does generally have a

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positive UV absorptive effect. Thus by using the reduced ZnO it may be possible to use less antioxidant or make the formulation longer lasting.

The organic solvents are typically from lower alcohols and polyols such as ethanol, isopropanol, propylene glycol, glycerin and sorbitol.

The fatty substances may consist of an oil or wax or mixture thereof, fatty acids, fatty acid esters, fatty alcohols, vaseline, paraffin, lanolin, hydrogenated lanolin or acetylated lanolin.

The oils are typically from animal, vegetable, mineral or synthetic oils and especially hydrogenated palm oil, hydrogenated castor oil, vaseline oil, paraffin oil, Purcellin oil, silicone oil and isoparaffin.

The waxes are typically animal, fossil, vegetable, mineral or synthetic waxes. Such waxes include beeswax, Carnauba, Candelilla, sugar cane or Japan waxes, ozokerites, Montan wax, microcrystalline waxes, paraffins or silicone waxes and resins.

The fatty acid esters are, for example, isopropyl myristate, isopropyl adipate, isopropyl palmitate, octyl palmitate, C₁₂-C₁₅ fatty alcohol benzoates ("FINSOLV TN" from FINETEX), oxypropylenated myristic alcohol containing 3 moles of propylene oxide ("WITCONOL APM" from WITCO), capric and caprylic acid triglycerides ("MIGLYOL 812" from HULS).

The compositions may also contain thickeners such as cross-linked or non cross-linked acrylic acid polymers, and particularly polyacrylic acids which are cross-linked using a polyfunctional agent, such as the products sold under the name "CARBOPOL" by the company GOODRICH, cellulose, derivatives such as methylcellulose, hydroxymethylcellulose, hydroxypropyl methylcellulose, sodium salts of carboxymethyl cellulose, or mixtures of cetylstearyl alcohol and oxyethylenated cetylstearyl alcohol containing 33 moles of ethylene oxide.

When the compositions of the present invention are sunscreens they may be in the form of, for example, suspensions or dispersions in solvents or fatty substances or as emulsions such as creams or milks, in the form of ointments, gels, solid sticks or aerosol foams. The emulsions may further contain anionic, nonionic, cationic or

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amphoteric surface-active agents. They may also be provided in the form of vesicular dispersions of ionic or nonionic amphiphilic lipids prepared according to known processes.

The following Examples further illustrate the present invention.

5 The degradation of sunscreen formulations was assessed as follows:

Methods:

Preparation of sample

Cut two strips of polythene 10mm x 25mm and 12.5mm thick.

10 Lay the polythene strips 20mm apart on the centre of a quartz slide.
Pipette a drop of about 30ml of sunscreen preparation onto the centre of the slide.
Carefully lay a second quartz slide on top of the sample and squeeze the slides together at the polythene strips thus providing a specimen 12.5μm thick. Take care to avoid air bubbles.

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Illumination

Use a Xenon lamp filtered with a Schott WG320 filter to carry out illuminations. Take a base reading of light output using a spectroradiometer calibrated between 290 and 400 nm.

Measure the light intensity (290-400nm) through a sample of water to use as a blank (Iq). The intensity over the range 290 - 400 nm is typical of that found in moderate latitudes in mid-summer.

Measure the light intensity (290-400nm) through the sample (It) at time 0 - as soon as it is put under the light - and then every 10 minutes for 1 hour.

At the end of the experiment take another base reading of light output to ensure that the light source has remained steady.

Calculations

Calculate the transmission (K) of the sunscreen film at each individual wavelength:

30 K = It / Iq

This can be used to plot wavelength vs transmission at each timepoint and shows the increase in transmission of an individual sunscreen during illumination.

The loss of light absorption (D) by the sunscreen at each individual wavelength is

calculated as the proportion of the absorption of the sunscreen at T=0 still remaining
at T=t:

$$D = K0/Kt$$

This can be used plot wavelength vs loss of light absorption. This plot allows comparisons to be made between different sunscreen preparations.

10 By measuring the area under this curve at each time point the rate of change of the total UVA absorption can also be calculated.

Formulations

Commercial sunscreen Factor 10. This has the following ingredients. The ingredients in italics are the active sunscreen agents.

Aqua

Ethyl hexyl methoxy cinnamate

Glycerin

20 Ceteareth-20

Butylene glycol dicaprylate/dicaprate

C12-15 alkyl benzoate

Glycerol stearate

Ethylhexyl triazone

25 Butyl methoxydibenzoylmethane

Phenoxyethanol

Cetyl palmitate

Cetearylalcohol

Ceteareth-12

30 PVP/hexadecane copolymer

Phenyl/benzimidazole sulphonate

Tocophenyl acetate

Methyl paraben

Ethylhexylglycerin

5 Trisodium EDTA

PEG-4 laurate

PEG-4 dilaurate

PEG-4

Iodopropynyl butylcarbamate

10 BHT

Perfume

This formulation was modified by the incorporation of ordinary or reduced ZnO of similar physical properties at 5% and compared. These materials were irradiated as described. The UVA absorption was recorded as a function of time to a total of 60 minutes. Each formulation containing reduced or ordinary zinc oxide showed about 2% transmission at time zero. The reduced zinc oxide however showed a reduced rate of loss of UVA absorption as a function of UV light exposure with a rate of loss of about 12% for ordinary zinc oxide and rate of loss of about 8% for reduced zinc oxide.

-13-**CLAIMS** A cosmetic UV sunscreening composition which comprises an 1. amount of one or more organic components which are photosensitive and/or which are degraded by another ingredient of the composition, optionally together with an amount of TiO2 and/or ZnO and an amount of reduced ZnO, this composition having a rate of loss of UV absorption at least 5% less than that of a composition having the same formulation except that it does not contain the reduced ZnO. A composition according to claim 1 which comprises 0.5 to 20 mole % by weight of reduced ZnO. 10 A composition according to claim 1 or 2 wherein the doped material has a particle size from 1 to 200 nm. A composition according to any one of the preceding claims wherein the reduced zinc oxide is once obtained by heating zinc oxide in a mixture of hydrogen and an inert gas. 15 A composition according to any one of the preceding claims wherein 5. one or more of the said organic components is a UV sunscreen agent. 6. A composition according to claim 5 wherein the organic sunscreen agent absorbs UV light in the UVA region. 7. A composition according to claim 5 or 6 wherein the organic 20 sunscreen agent is a paraaminobenzoic acid, ester or derivative thereof, a methoxy cinnamate ester, a benzophenone, a dibenzylomethane, an alkyl-β,β-phenyl acrylate, a triazine, a camphor derivative, an organic pigment, a silicone based sunscreen agent or 2-phenylbenzimidazoyl-5 sulphonic acid or phenyldibenzimidazoyl sulphonic acid. 25 8. A composition according to any one of the preceding claims wherein the said rate of loss of UV absorption is a rate of loss of UVA absorption. A composition according to any one of the preceding claims wherein the rate of change of the ratio of the loss of UVA absorption to the loss of UVB absorption is less than that of a composition of the same formulation except that the 30 ZnO present is not reduced. 10. A composition according to claim 9 wherein the rate of change of the

ratio is greater because the rate of loss of UVA absorption is reduced.

- 11. A composition according to any one of the preceding claims wherein the organic sunscreen agent is one which is degraded by ZnO.
- 12. A composition according to any one of the preceding claims which comprises 0.1% to 20% by weight of organic sunscreen agent(s).
 - 13. A composition according to any one of the preceding claims which contains one or more of a fatty substance, organic solvent, silicone, thickener, demulsant, UVB sunscreen agent, antifoaming agent, moisturising agent, perfume preservative, surface activation filler, sequestrant, anionic, cationic, nonionic or amphoteric polymer, propellant, alkalising or acidifying agent, colorant or metal oxide pigment.
 - 14. A composition according to any one of the preceding claims which is a sunscreen.
- 15. A composition according to any one of the preceding claims which is in the form of a lotion, gel, dispersion, cream, milk, powder or solid stick.
 - 16. A composition according to claim 1 substantially as hereinbefore described.
 - 17. Use of reduced ZnO to reduce the concentration of one or more organic UV sunscreen agents or other ingredient which is photosensitive and/or is degraded by another ingredient in a cosmetic UV screening composition.

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- 18. Use of reduced ZnO to reduce the rate of loss in UV absorption of a sunscreen composition.
- 19. Use of reduced ZnO to reduce the rate of change of the ratio of the loss of UVA absorption to the loss of UVB absorption in a cosmetic UV screening composition which comprises one or more organic components which are photosensitive and/or which are degraded by another ingredient of the composition in a relation a composition of the same formulation except that the ZnO present is not reduced.
- 20. A method of increasing the effectiveness of an organic UV
 30 sunscreening composition, which comprises one or more components which are

photosensitive and/or are degraded by another ingredient of the composition which comprises incorporating into the composition reduced ZnO.

ABSTRACT

A cosmetic UV sunscreening composition is described which comprises an amount of one or more organic components which are photosensitive and/or which are degraded by another ingredient of the composition, optionally together with an amount of TiO₂ and/or ZnO and an amount of reduced ZnO, this composition having a rate of loss of UV absorption at least 5% less than that of a composition having the same formulation except that it does not contain the reduced ZnO.